Available online at www.sciencedirect.com
ScienceDirect
Journal of Molecular Structure 841 (2007) 110–117
Journal of MOLECULAR STRUCTURE
www.elsevier.com/locate/molstruc

Mono and polynuclear silver(I) complexes with thiosaccharine and triphenylphosphine or 2,2′-bipyridine. Synthesis, spectroscopic and structural characterization

Mariana Dennehy [a], Oscar V. Quinzani [a,*], Michael Jennings [b]

[a] Departamento de Química, Universidad Nacional del Sur, Avda. Alem 1253 B8000CPB Bahía Blanca, Argentina
[b] X-ray Structures Western, Chemistry Department, University of Western Ontario, London, Ont., Canada N6A 5B7

Received 11 September 2006; received in revised form 28 November 2006; accepted 30 November 2006

Abstract

Reaction of $Ag_6(tsac)_6$ ($tsac^- =$ thiosaccharinate anion) with PPh_3 and 2,2′-bipyridine (bipy) ligands give rise to three new silver-thiosaccharinate complexes, $[Ag(tsac)(PPh_3)_3]$, $[Ag_4(tsac)_4(PPh_3)_3]$, and $[Ag_2(tsac)_2(bipy)_2]$. Their crystal structures established by single-crystal X-ray diffraction and IR spectroscopic characterizations are reported here. In each complex a singular coordination mode for the thiosaccharinate ligands is observed. The most important features of the different coordination modes of the thionates are discussed.

Keywords: Silver(I) complexes; Heterocyclic thiones; Thiosaccharine; Crystal structure

1. Introduction

Silver (I) complexes with thiolate or heterocyclic thioamidate (thionate) ligands have been widely studied because they have shown a great tendency to form cluster and polymer structures [1–3] with potential application in catalysis and inorganic–organic hybrid conductors [2c]. A considerable amount of work has been centered around the coordination chemistry of heterocyclic thiones, versatile S,N ligands capable to bind to metals in a great variety of coordination forms: *N* or *S*-monodentate, μ_2-*S*-bridge, *N*,*S*-chelate, μ_2-*N*,*S*-bridge, μ_2-*N*,*S*-(η^2-*S*)-bridge, μ_3-*N*,*S*-(η^2-*S*, η^1-*N*)-bridge. A rich field of mononuclear, binuclear and complex polynuclear coordination compounds has then developed [3]. Several reviews dealing with the coordination of these heterocyclic thione ligands have been published since the first leading works of E.S. Rapper [4]. In the last few years, with the aim to further exploring the coordination behavior of thiosaccharine (the thione form of saccharine, $C_6H_4S(O)_2NHC(S)$) our research group have studied several new compounds of Cd(II), Tl(I), and Pd(II) [5]. This work was recently reviewed by E. Baran and V. Yilmaz [6]. As it is well known for other heterocyclic thiones, thiosaccharine has a tautomeric equilibrium in solution and in its thiol form can act as a good coordinating agent for soft metals, building mononuclear and polynuclear structures with or without the presence of additional ligands. Recently, our research group has structurally characterized polynuclear Ag(I) and Cu(I) thiosaccharinates, having hexanuclear $[Ag_6(tsac)_6]$ and tetranuclear $[Cu_4(tsac)_4]$ molecular units, respectively [7]. In these compounds the thiosaccharinate anion acts as a bridging tridentate ligand, with the exocyclic sulfur atom and the endocyclic nitrogen atom simultaneously bonded to three metal atoms, joining the corners of triangular faces of the polyhedra formed by the metal atoms. Hexanuclear and tetranuclear clusters are common structures in the coordination chemistry of silver(I), and depending on the nature of the ligands and on electronic demands of the metal d^{10} closed electronic configuration, coordination numbers can range from 2 to 5. Usually, trisubstituted phosphine, bipyridine or

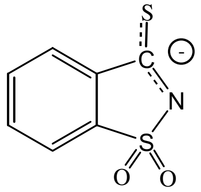
---

[*] Corresponding author. Tel.: +54 291 4595159; fax: +54 291 4595160.
E-mail address: quinzani@criba.edu.ar (O.V. Quinzani).

0022-2860/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2006.11.071

phenanthroline molecules are used to control the stereochemistry and/or nuclearity of silver complexes, and when halogenides or thiolates are the counterions, they can also coordinate to metal centers as monodentate or bridged bidentate ligands [1,8–13]. Bowmaker et al. have characterized a number of silver-2,2′-bipyridine complexes with different oxyanions [14]. By controlling the experimental conditions, diverse structures, like the tetranuclear $(PPh_3)_2Ag_4(MT)_4$ (MT = 2-mercaptothiazoline) [11], dinuclear $[Ag(PPh_3)(bzimtH_2)Br]_2$ ($bzimtH_2$ = benz-1,3-imidazoline-2-thione) [12] and mononuclear $[Ag(PPh_3)_2(py2SH)Cl]$ (py2SH = pyridine-2-thione) [13] compounds have been obtained by other authors from Ag–triphenylphosphine–thione mixtures.

With the aim to analyze the influence of these bulky ligands on the molecular geometry of ternary silver(I) thiosaccharinate complexes, and on the coordination modes of the thiosaccharine ligand, three new silver complexes are reported in the present study. These complexes display different coordination modes for the thiosaccharinato ligand: tris(triphenylphosphine)-η^1-*S*-(thiosaccharinato)silver(I), $[Ag(tsac)(PPh_3)_3]$, bis(2,2′-bipyridine)bis-μ_2-*S*-(thiosaccharinato)-disilver(I), $[Ag_2(tsac)_2(bipy)_2]$, and tris (triphenylphosphine)tetrakis-μ_3-*S*,*N*-(thiosaccharinato)-tetrasilver(I), $[Ag_4(tsac)_4(PPh_3)_3]$.


tsac

2. Experimental

2.1. Materials and chemical analysis

Thiosaccharine (Htsac) was prepared by reaction of saccharine (Mallindkrodt) with Lawesson's reagent (Fluka) in toluene, according to the procedure described by Schibye et al. [15]. Ag(tsac) (**1**) was prepared as a yellow solid by the reaction of $AgNO_3$and thiosaccharine in acetonitrile, in molar ratio 1:1 (yield: 71%) and recrystallized in the same solvent [7].

The white crystalline substance $[Ag(PPh_3)_4]BF_4$ was obtained by the addition of $Ag(BF_4)$ (Aldrich) to a concentrated solution of PPh_3 in dried THF, in a Ag/PPh_3 molar ratio of 1:5. Solvents used in this work were of analytical grade and dried by known procedures [16]. The percent elemental composition analyses were performed at INQUIMAE (Facultad de Ciencias Exactas y Naturales, UBA, Argentina).

2.2. Synthesis of $[Ag(tsac)(PPh_3)_3]$ (**2**)

A pale yellow solid was obtained by slow addition of complex (**1**) in a PPh_3 solution in acetonitrile under constant stirring, at room temperature. The solid was collected by filtration and washed with small amounts of diethyl ether. Varying the stoichiometry of the reaction from a Ag/PPh_3 molar ratio 1:3 [Ag(tsac) 0.015 g (0.05 mmol)/ PPh_3 0.039 g (0.15 mmol)] to 1:2 [Ag(tsac) 0.012 g (0.04 mmol)/ PPh_3 0.021 g (0.08 mmol)] yielded the same solid. The compound was recrystallized by slow evaporation of saturated solutions of the complex in acetonitrile at room temperature. Yellow single crystals suitable for X-ray diffraction study were formed during evaporation. The compound was air and light-stable.

The same compound was also obtained as a microcystalline powder from the reaction of equimolar amounts of $[Ag(PPh_3)_4]BF_4$ (0.072 g, 0.060 mmol) and thiosaccharine (0.012 g, 0.060 mmol) dissolved in methanol–ethanol (3:1) mixtures (16 ml).

2.3. Synthesis of $[Ag_2(tsac)_2(bipy)_2]$ (**3**)

The complex was prepared by slow addition of a Htsac solution (0.020 g, 0.10 mmol) in CH_3CN to a $AgNO_3$ solution (0.016 g, 0.10 mmol) in CH_3CN containing also 2,2′-bipyridine (0.016 g, 0.10 mmol). The resulting clear yellow solution was kept in the darkness at room temperature and a day later yellow crystals were formed. Yield: 55%. Anal. Calcd. for $C_{34}H_{24}N_6O_4S_4Ag_2$ (%) C, 44.2; N, 9.1; H, 2.6; S, 13.9%. Found: C, 45.1; N, 8.8; H, 2.4; S, 13.8%. The compound was air and light-stable. Some of the formed crystals were of a quality suitable for single-crystal X-ray diffraction study. Compound (**3**) was also obtained as yellow crystals by slow diffusion of CH_2Cl_2 in a solution containing equimolar amounts of complex (**1**) (0.030 g, 0.10 mmol) and 2,2′-bipyridine (0.016 g, 0.10 mmol) in DMSO.

Attempts to obtain 4,4′-bipyridine derivates of Ag(tsac) by using the appropriate stoichiometric amount of the N-donor ligand were unsuccessful. The diamine favored the dissolution of **1** but in the crystallization processes the last complex being always recovered.

2.4. Synthesis of $[Ag_4(tsac)_4(PPh_3)_3]$(**4**)

The new crystalline substance was prepared by the reaction of (**1**) and PPh_3 in acetonitrile in a molar ratio Ag/PPh_3 1:1 (Ag(tsac) 0.024 g, 0.080 mmol and PPh_3 0.020 g, 0.080 mmol), in the presence of 4,4′-bipyridine (0.012 g, 0.080 mmol). The resulting clear solution was kept at room temperature in the darkness for 24 h, giving yellow single crystals. After a few days, some of the crystals loose their original quality. Then the results of several chemical analyses not being reproducible.

2.5. Spectroscopic measurements

Infrared spectra were recorded between 4000 and 400 cm^{-1} on a Nicolet Nexus FTIR spectrophotometer using the KBr pellet technique. Spectra obtained from suspensions of the powdered samples in Nujol gave identical results. The electronic absorption spectra of the solid state complexes dispersed in KBr discs were recorded on a Cecil CE 2021 spectrophotometer in the range of 200–550 nm. The ^{1}H, ^{13}C and ^{31}P-NMR spectra of $CDCl_3$ solutions, at 300 K, were recorded on a Multinuclear Bruker ARX-300 equipment.

2.6. Crystal structure determinations

Data were collected at room temperature (25 °C) on a Nonius Kappa-CCD area detector diffractometer with COLLECT (Nonius B.V., 1997–2002). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN (Otwinowski and Minor, 1997). The absorption correction was applied using HKL2000 DENZO-SMN (SCALEPACK). The crystal data and refinement parameters for the three complexes are listed in Table 1.

The SHELXTL/PC V6.14 for Windows NT (Sheldrick, G.M., 2001) [17] suite of programs was used to solve the structure by direct methods. Subsequent difference Fourier syntheses allowed the remaining atoms to be located. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. Complex (**3**) was situated across a center of symmetry and thus, only half of the molecule was resolved and refined.

3. Results and discussion

3.1. FT-IR spectra

The solid state FT-IR spectra of the complexes provide information regarding the coordination mode of the thione ligand and confirm the presence of the secondary ligands. The most interesting bands to be analyzed are those related to vibrations of the five membered ring of the thiosaccharinate anion, located between 1500 and 400 cm^{-1}. There are no significant differences for the bands corresponding to vibrations of the thione benzenic ring after coordination. The disappearance of the ν(N–H) band of the protonated thiosaccharine is confirmed in combination with the lack of ν(SH) band at 2500-2600 cm^{-1}, indicating that the thione ligand is in the deprotonated form in these complexes [5a,18]. Table 2 reports the IR vibrational assignments for the thiosaccharinate moieties. Those assignments are based on the general informa-

Table 1
Crystallographic data and structure refinement for complexes $[Ag(tsac)(PPh_3)_3]$ (**2**), $[Ag_2(tsac)_2(bipy)_2]$ (**3**) and $[Ag_4(tsac)_4(PPh_3)_3]$ (**4**)

Identification code	(**2**)	(**3**)	(**4**)
Empirical formula	$C_{61}H_{49}AgNO_2P_3S_2$	$C_{34}H_{24}Ag_2N_6O_4S_4$	$C_{82}H_{61}Ag_4N_4O_8P_3S_8$
Formula weight	1092.91	924.57	2011.22
Temperature	298(2) K	298(2) K	301(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	Pbca	P-1	P-1
Unit cell dimensions	$a = 19.8680(3)$ Å	$a = 8.189(2)$ Å	$a = 13.8042(12)$ Å
	$b = 20.4812(3)$ Å	$b = 8.887(2)$ Å	$b = 15.9230(11)$ Å
	$c = 25.4391(3)$ Å	$c = 12.313(4)$ Å	$c = 19.6305(18)$ Å
	$\alpha = 90°$	$\alpha = 88.40(2)°$	$\alpha = 84.422(5)°$
	$\beta = 90°$	$\beta = 80.24(2)°$	$\beta = 84.107(4)°$
	$\gamma = 90°$	$\gamma = 72.10(2)°$	$\gamma = 89.343(4)°$
Volume	10351.7(2) Å^3	840.1(4) Å^3	4271.7(6) Å^3
Z	8	1	2
Density (calcul.)	1.403 Mg/m^3	1.828 Mg/m^3	1.564 Mg/m^3
Abs. coefficient	0.608 mm^{-1}	1.464 mm^{-1}	1.210 mm^{-1}
F(000)	4496	460	2012
Crystal size	0.40 × 0.38 × 0.22 mm^3	0.75 × 0.15 × 0.05 mm^3	0.15 × 0.13 × 0.03 mm^3
Theta range for data collection	2.55–25.03°	2.90–25.02°	2.56–25.03°
Index ranges	$-23 \leqslant h \leqslant 23$,	$9 \leqslant h \leqslant 9$,	$-16 \leqslant h \leqslant 13$,
	$-24 \leqslant k \leqslant 24$,	$-10 \leqslant k \leqslant 10$,	$-18 \leqslant k \leqslant 18$,
	$-30 \leqslant l \leqslant 30$	$-10 \leqslant l \leqslant 14$	$-23 \leqslant l \leqslant 23$
Reflections collected	95643	4247	35481
Independent reflect.	9131 [R(int) = 0.062]	2675 [R(int) = 0.044]	14951 [R(int) = 0.095]
Completeness to theta	= 25.03° 99.8%	= 25.02° 90.1%	= 25.03° 99.1%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.8753 and 0.7929	0.9304 and 0.4064	0.9704 and 0.8393
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	9131/0/523	2675/0/226	14951/0/874
Goodness-of-fit on F^2	1.023	1.057	0.992
Final R indices [$I > 2$sigma(I)]	$R1 = 0.0399$, w$R2 = 0.0990$	$R1 = 0.0469$, w$R2 = 0.1178$	$R1 = 0.0760$, w$R2 = 0.1298$
R indices (all data)	$R1 = 0.0698$, w$R2 = 0.1135$	$R1 = 0.0707$, w$R2 = 0.1297$	$R1 = 0.2376$, w$R2 = 0.1751$
Largest diff. peak and hole	0.470 and −0.942 e Å^{-3}	0.631 and −0.871 e Å^{-3}	0.575 and −0.588 e Å^{-3}

Table 2
FT-IR spectra assignment for the thiosaccharinate absorption bands of complexes (**1**), (**2**), (**3**) and (**4**)

Assignments	(**1**)	(**2**)	(**3**)	(**4**)
ν(CN), ν(Φs)	1440m[a]	(1398)[b]	1411m	(1435)[b]
$\nu_{as}(SO_2)$	1334vs	1296vs	1302s	1319s
$\nu_s(SO_2)$, ν(CC)	1170vs	1155s/ 1148s	1159vs/1151vs	1166vs
$\nu_s(SO_2)$, $\delta(\phi SN)$	1126m	1117m	1123m	1123m
ν(CS), δ(CNS)	1000vs	1006m	997s	1003s
ν(NS), δ(CCC)	800s	814m	795s	800m
$\gamma(SO_2)$, $\delta(\phi CN)$	628w	623w	626m	626w
$\delta w(SO_2)$, δ(CS)	555m	553w	553m	555m
γ(CCS)	540w	538vw	536m	536w

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

[b] Overlapped with neutral ligand bands.

tion analyzed and discussed in previous papers [5,19] and on the theoretical calculations performed by I. Binev et al. and G. Jovanovski et al. [20].

In all the new compounds the stretching of the C–N and C–S_{exo} (exo: exocyclic) bonds lie at greater and lower frequencies, respectively, than for the “free” anion in ammonium thiosaccharinate, (NH_4)tsac [ν(CN): 1340 cm^{-1} and ν(CS): 1014 cm^{-1}] [21] or potassium thiosaccharinate, K(tsac) [ν(CN): 1338 cm^{-1} and ν(CS): 1016 cm^{-1}] [5e]. This is in accordance with anionic ligands coordinated in the thiolato form in the solid complexes. The possible participation of the nitrogen atom in the coordination is not clearly indicated by the IR data. The spectra show the expected strong absorptions produced by the C-H bonds and the skeletal vibrations of the coordinated triphenylphosphine [22] and 2,2′-bipyridine [23] ligands. For complexes (**2**) and (**4**) some thiosaccharinate absorptions are masked by the strong bands of the PPh_3.

3.2. Electronic and NMR spectra

The electronic absorption spectra of the solid complexes (**2**) and (**4**) (KBr discs) show two intense bands at 220 and 270 nm, and a broad band with a maximum at 335–358 nm. The first two bands can be attributed to the $\pi \rightarrow \pi^*$ transitions of the phenyl groups in the phosphine ligands. The lower energy band lies in the spectral region for the expected $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ (C–S) transitions in thiosaccharine and other thiones [4d]. The electronic spectra for complex (**3**) show three peaks at 203, 297 and 367 nm. The first two corresponding to transitions of the 2,2′-bipy ligands and the later to the thionates [24].

In the ^{1}H-NMR spectra of $[Ag(tsac)(PPH_3)_3]$ complex, the signals due to the triphenylphosphine molecules lie in the range 7.07–7.34 ppm (m,46H), partially mixed with the resonances of one of the protons of the thiosaccharinate anion. Between 7.36 and 7.90 ppm, three of the thiosaccharinate-proton signals appear, centered at 7.41(m,1H), 7.55 (d,1H) and 7.85 (d,1H), upfield shifted from the corresponding resonances of Pd(II) thiosaccharinate [5f]. In the $^{31}P\{^1H\}$ spectra of complex **2** only a broad singlet at 55.72 ppm is observed, downfield shifted from the free ligand. It indicates that the ligands strongly coordinate to the silver atoms and there is only one species in the $CDCl_3$ solution. The existence of a broad singlet instead of the doublet or doublet–doublet signals expected for a P-atom coordinated to a silver nucleus, is presumed to be a consequence of the existence of a rapid ligand-exchange equilibrium at room temperature [25]. In the ^{13}C-NMR spectra of complex **2** the five signals centered at 120.44, 126.04, 135.45, 138.77 and 189.17 ppm can be assigned to carbon atoms resonances of the thiosaccharinate ligands [5f]. The last signal, corresponding to the thiocarbonilic carbon atoms, is downfield shifted from the free ligand, indicating that the anions are coordinated to the silver centers in solution [5f]. The PPh_3-carbon signals lie in the range 128.7–134.5 ppm, mixed with the resting two resonances of the thiosaccharinate anions.

In the ^{1}H-NMR spectra of the complex $[Ag_2(tsac)_2(2,2'\text{-}bipy)_2]$ in CDCl3 solutions, the characteristic signals of the 2,2′-bipyridine ligands lie at 7.59 (mixed with a $tsac^-$ resonance), 7.98 (dt,4H), 8.20 (dd,4H) and 8.80 (dd,4H) ppm. The pattern of the signals and their chemical shifts indicate the coordination of the bipyridines to the silver atoms [26]. Three of the thiosaccharinate-proton resonances are centered at 7.78 (m,1H), 7.90 (d,1H) and 8.11 (d,1H) and it cannot be concluded if complex **3** is dimeric in solution or changes to the mononuclear structure observed for other [AgL(2,2′-bipy)] complexes [26].

To understand the effect of the presence of 4,4′-bipyridine in the synthesis of the $[Ag_4(tsac)_4(PPh_3)_3]$ complex, the ^{1}H-NMR and $^{31}P\{^1H\}$-NMR spectra of equimolar mixtures of Ag(tsac) (**1**), triphenylphosphine and 4,4′-bipyridine in CDCl3 solutions were obtained. Much of the proton signals of the substances lie in the range between 7.3 and 7.8 ppm. In the mixture of resonances, a characteristic doublet-doublet signal at 7.76 ppm can be assigned to the H2,H2′ protons of 4,4′-bipyridine. The other doublet-doublet resonances of the H3,H3′ protons appears at 8.96 ppm. Then, both bipyridine signals are downfield shifted from the free ligand (7.44 and 8.65 ppm). The appearance of only two bipyridine signals, both downfield shifted indicates that in solution, 4,4′-bipyridine acts as a bridge between silver atoms [27]. The $^{31}P\{^1H\}$ spectra of the mixture in $CDCl_3$ solutions show only a broad singlet at 62.13 ppm and a very small signal at 79.91 ppm. Both phosphorus resonances are downfield shifted from the signals of PPh_3 molecules in complex **2**, a expected effect when the number of phosphines coordinated to the same metal center diminished [28]. The observation of two phosphorus signals indicates the existence of a mixture of species in solution. Then, the 4,4′-bipyridine molecules act as ligands in solution and the PPh_3 molecules are tightly bonded to the metal centers. But in the process of crystallization of complex **4**, the bipyridine ligand leaves the silver coordination spheres. This phenomena may be responsible for the asymmetry of the molecule, with only three silver nuclei coordinated by PPh_3 moieties.

3.3. Crystal structures

3.3.1. Complex $[Ag(tsac)(PPh_3)_3]$ (2)

X-ray structure analysis of complex (**2**) reveals that this mononuclear compound crystallizes in the orthorhombic space group Pbca, with eight molecules in the unit cell. A selection of bond lengths and angles of the compound are listed in Table 3 and a thermal ellipsoid plot of its structure is shown in Fig. 1. Consideration of the angles around the central metal atom indicate than the Ag cation is located in the center of a distorted tetrahedron. The silver coordination sphere is formed by one S atom of a monocoordinated thionate and three P atoms of triphenylphosphine molecules. The Ag–S distance of 2.5939(10) Å, lies in the upper side of the range for silver thiolate or thionate complexes [10] and is very similar to the distances observed for neutral thiones coordinated to silver atoms, such as $[Ag(PPh_3)_2$ (py2SH)Cl] (Ag–S: 2.625 Å) [13] or $[Ag_2(\mu\text{-}dppen)_3(pymtH)_2](NO_3)_2$ (Ag–S: 2.5660/2.5923 Å) [dppen: bis(diphenylphosphine)ethene, HpymyH: pyrimidine-2-thione] [29]. Notwithstanding the volume of the phosphines forces the Ag–S bond to lengthen, the thiosaccharinate-silver interaction is strong enough to allow the replacement of one PPh_3 molecule from the $[Ag(PPh_3)_4]^+$ cation, even in the presence of an excess of the phosphine ligand. The three Ag–P distances (2.522(8), 2.575(8) and 2.676(8) Å), are very similar to the values found for other complexes containing tetra coordinated silver atoms bonded to three phosphorus atoms like $Ag(PPh_3)_3I$ [*d*(Ag–P) = 2.533, 2.559 and 2.681 Å] [8a]. Shorter Ag–PPh_3 bond lengths have been observed in silver thiolates or thionates with only one or two phosphine molecules bonded to the metal centers [8b,24,30,31]. The deviations of the P–Ag–P angles from an ideal tetrahedral geometry [112.58(3), 113.35(3) and 112.03(3)°] may be attributed to steric interactions between the bulky PPh_3 ligands and are in accordance with the observed differences between Ag–P bond lengths.

Table 3
Selected bond lengths [Å] and angles [°] for $[Ag(tsac)(PPh_3)_3]$ (**2**)

Ag–P2	2.5226(8)	Ag–P3	2.6765(8)
Ag–P(1)	2.5752(8)	S1–C2	1.678(3)
Ag–S(1)	2.5939(10)	C2–N3	1.320(4)
P2–Ag–P1	112.58(3)	P1–Ag–P3	112.03(3)
P2–Ag–S1	129.28(3)	S1–Ag–P3	93.20(3)
P1–Ag–S1	94.01(3)	C2–S1–Ag	124.68(12)
P2–Ag–P3	113.35(3)		

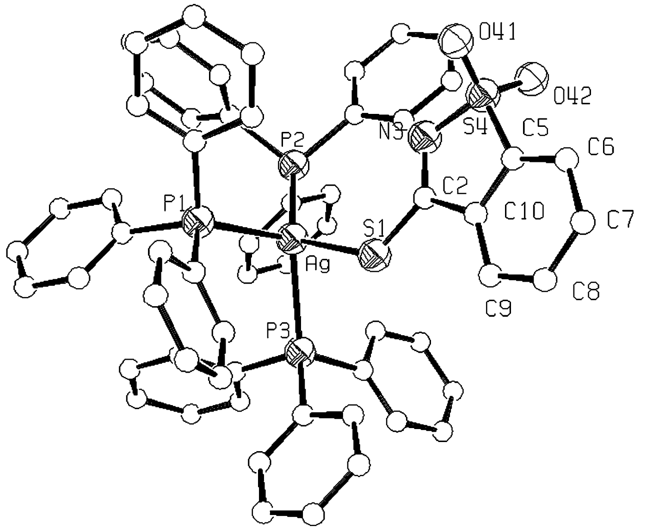


Fig. 1. ORTEP drawing of the molecular structure of $[Ag(tsac)(PPh_3)_3]$ (**2**) showing 50% probability ellipsoids. Hydrogen atoms and some atom-labellings are omitted for clarity.

The thiosaccharine ligand changes its structure after coordination. Upon deprotonation the thiocarbonile bond of Htsac (C=S: 1.622 Å) [18] becomes longer due to the negative charge delocalization over the S_{exo} atom [19], i.e. to a value of 1.666 Å in the ionic ammonium thiosaccharinate [21]. In the silver complex the monocoordination of the ligand through the exocyclic S atom makes the C2–S1 distance slightly longer (1.678(3) Å), although it is shorter than other monocoordinated thiosaccharinates, like $Cd(tsac)_2 \cdot H_2O$ (1.7083 Å) and $Cd(tsac)_2(bim)_2$ (1.7022/1.6965 Å) [5a,5d]. This fact reflects the already discussed lengthening of the Ag(I)–tsac interaction in the crowded $Ag(PPh_3)_3^+$ centers. It agrees as well with the IR positions of the bands corresponding principally to the stretching vibration of the C–S_{exo} bond, *ν*(CS), which appears at 1016 cm^{-1} in NH_4(tsac) and 1000 cm^{-1} in $Ag_6(tsac)_6$ and in the middle of the range, 1006 cm^{-1}, in $Ag(tsac)(PPh_3)_3$. The C–N bond distances are also within the expected limits: C2–N3 bond of 1.320(4) Å in complex (**2**) versus 1.312/1.314 Å in $Cd(tsac)_2(bim)_2$ [5d] and 1.334 Å in ammonium thiosaccharinate [21]. This is in agreement with the relative IR stretching frequencies, *ν*(CN), shown in Table 2.

Finally, the nine independent P–C bond distances (averaging 1.830 Å) are comparable to those observed in other Ag–phosphine complexes reported in the literature [13].

3.3.2. Complex $[Ag_2(tsac)_2(bipy)_2]$ (3)

Data for $[Ag_2(tsac)_2(bipy)_2]$ complex were consistent with a triclinic space group P(−1), with one molecule in the unit cell. The full complex is a simple centrosymmetric dinuclear molecule where the silver nuclei are held together by a Ag–Ag bond and two Ag–S–Ag bridges, using the exocyclic S atoms of the two thiosaccharinate anions. A thermal ellipsoid representation of the molecular structure is reported in Fig. 2. Selected bond length and angles of complex (**3**) are listed in Table 4.

Complex (**3**) can be described as a Ag_2S_2 parallelogram with the bipyridine molecules placed almost perpendicular to the first subunit (torsion angle Ag′–S1–Ag–N11: 142.93(14)°). The Ag–S bond lengths (2.5770(19) and 2.6305(18) Å) lie in the range of other dimeric or polymeric silver–thiol or –thione compounds, like $[Ag(PPh_3)(bzimtH_2)\ Br]_2$ (2.5548 Å) [12] and $[\{Ag(py2SH)_2\}BF_4]_n$ (2.555 and 2.680 Å) or $[Ag(py2S)]_n$ (2.424 and 2.647 Å) where the Ag_2S_2 subunits polymerize as infinite chains or sheets [2c]. The metal-metal separation (Ag–Ag′: 2.7884(12) Å) is shorter than the corresponding distance in

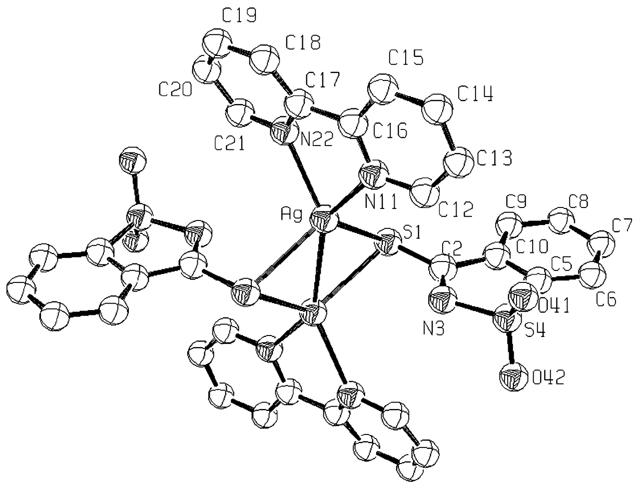


Fig. 2. ORTEP drawing of the molecular structure of $[Ag_2(tsac)_2(bipy)_2]$ (**3**) showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

metallic silver (2.88 Å [32]), and it can be considered as an effective Ag–Ag bond following the criteria of P. Pyykkö [33] and M. Jansen [34]. Although the closed d^{10} configuration of Ag(I) appears to make any intermetallic bonding between silver centers unnecessary [35a]. Very similar Ag–Ag separations have been found for one of the bonds, the shortest bond, in the polymeric $[Ag(pyS)]_n$ complex (2.799 Å) [2c].

The thiosaccharinate anions can be considered as planar species twisted with respect to the Ag_2S_2 unit by 98.70° and not coplanar between them (interplanar distance is approx. 0.10 Å). The twisted positions together with the great value of the S1–C1–N2 angle (125.5(4)°) put the endocyclic N atoms too far apart for any Ag–N interaction (Ag···N3 distance is 3.492 Å). The C–S_{exo} bond length (1.697 Å) is longer to the bond length found for the thiosaccharinate anion in complex (**2**) (1.678(3) Å). This is in agreement with the change from single bonded (η^1-S) mode in complex (**2**) to bridging (μ_2-S) in complex (**3**). Moreover, the C2–N3 bond length (1.310(7) Å) is a little shorter than in complex (**2**). Ag–N bonds in complex (**3**) (2.327(5) and 2.356(5) Å) are little longer than in other Ag(I)-2,2′-bipyridine containing complexes [14]. The two halves of 2,2′-bipyridine are quasi-coplanar, showing a interplanar dihedral angle of 16.3°, similar to the value 16.61° found for $AgNO_3$:bpy [14].

Table 4
Selected bond lengths [Å] and angles [°] for $[Ag_2(tsac)_2(bipy)_2]$ (**3**)

Ag–N11	2.327(5)	Ag–Ag#1	2.7884(12)
Ag–N22	2.356(5)	S1–C2	1.697(5)
Ag–S1	2.5770(19)	C2–N3	1.310(7)
Ag–S1#1	2.6305(18)		
S1–Ag–S1#1	115.26(5)	N11–Ag–S1#1	121.79(13)
S1–Ag–Ag#1	58.56(5)	N22–Ag–S1#1	106.34(12)
S1#1–Ag–Ag#1	56.70(4)	N11–Ag–Ag#1	145.10(13)
Ag–S1–Ag#1	64.74(5)	N22–Ag–Ag#1	143.92(12)
N11–Ag–N22	70.66(17)	C2–S1–Ag	101.9(2)
N11–Ag–S1	110.48(13)	C2–S1–Ag#1	102.8(2)
N22–Ag–S1	125.97(13)	N3–C2–S1	125.5(4)

Finally, in complex (**3**) one can observe that there are no significant intermolecular packing interactions worth commenting on.

3.3.3. *Complex $[Ag_4(tsac)_4(PPh_3)_3]$ (4)*

The crystal system for complex (**4**) was found to be triclinic P(−1), with a single molecule, and some voids in the asymmetric unit. Selected bonds and angles for (**4**) are listed in Tables 5 and 6, respectively. The molecular structure of the complex is shown in Fig. 3. The metal center arrangement inside the cluster do not conform to a regular polyhedra, indeed it is partway between a tetrahedron and a regular "butterfly" structure. Finer detail of the inner molecular arrangement of the Ag, P, S_{exo} and N atoms is reported in Fig. 4. The metal-metal distances are in the range 2.952–4.349 Å, and only two distances, namely Ag1–Ag2 and Ag1–Ag3, are considered weak silver-silver bonds [33]. The four faces of the "tetrahedron" are capped by thiosaccharinate ligands tri-coordinated in a μ_3-S,N (η^2-S; η^1-N) six electron donor system. The apparently regular structure becomes distorted by the presence of triphenylphosphine ligands at only three of the four metal centers. Silver atom Ag4 has a flattened tetrahedral PS_2N environment; Ag2 and Ag3 have similar asymmetric coordination spheres conformed by a P atom, two S_{exo} atoms, one N atom and the Ag1 metal center, while Ag1 is in the center of a distorted trigonal bipyramid formed by two S_{exo} atoms, one N atom and two silver centers (Ag2 and Ag3). As can be expected, bond distances around Ag1 atom are shorter than those observed for the triphenylphosphine bonded atoms. Notwithstanding, all the inner cluster bond lengths and the Ag–PPh_3 distances are within the values observed for other silver–thiolate and silver–thiolate–PPh_3 complexes [2c,3b,35b–38]. The chemistry of binary and ternary silver-thiolate compounds shows a great variety of regular or irregular metal-ligand polyhedric structures. When PPh_3 is the third ligand, regular arrangements such as $(PPh_3)_2Ag_4(MT)_4$ [11], or irregular structures, such as the distorted "chair" in $[Ag_4(SPh)_4(PPh_3)_4]$ [10] or the highly distorted octahedron in the $[Ag_6(SC_6H_4Cl)_6(PPh_3)_5]$ cluster [35b], has also been observed.

The thiosaccharinate C–S_{exo} bond lengths are longer than those observed in complex (**3**) showing a stronger

Table 5
Selected bond lengths [Å] for $[Ag_4(tsac)_4(PPh_3)_3]$ (**4**)

Ag1–Ag3	2.9521(12)	Ag4–N43	2.311(8)
Ag1–Ag2	2.9998(11)	Ag4–P4	2.559(3)
Ag1–N13	2.270(8)	Ag4–S21	2.582(3)
Ag1–S31	2.427(3)	Ag4–S11	2.624(3)
Ag1–S41	2.479(3)	S11–C12	1.717(11)
Ag2–N23	2.313(9)	C12–N13	1.305(12)
Ag2–P2	2.496(3)	S21–C22	1.732(10)
Ag2–S11	2.618(3)	C22–N23	1.303(12)
Ag2–S31	2.679(3)	S31–C32	1.689(10)
Ag3–N33	2.331(8)	C32–N33	1.302(11)
Ag3–P3	2.481(3)	S41–C42	1.718(12)
Ag3–S21	2.595(3)	C42–N43	1.310(12)
Ag3–S41	2.660(3)		

Table 6
Selected angles [°] for [$Ag_4(tsac)_4(PPh_3)_3$] (**4**)

Ag3–Ag1–Ag2	93.88(3)	S31–Ag2–Ag1	50.20(6)
N13–Ag1–S31	119.2(2)	N33–Ag3–S21	103.80(19)
N13–Ag1–S41	104.1(2)	N33–Ag3–S41	113.3(2)
S31–Ag1–S41	131.89(10)	S21–Ag3–S41	123.38(10)
N13–Ag1–Ag3	141.3(2)	P3–Ag3–Ag1	145.81(8)
S31–Ag1–Ag3	94.05(7)	S41–Ag3–Ag1	52.11(6)
S41–Ag1–Ag3	57.87(7)	N33–Ag3–P3	119.5(2)
N13–Ag1–Ag2	88.5(2)	P3–Ag3–S21	103.51(10)
S31–Ag1–Ag2	58.02(7)	P3–Ag3–S41	93.90(10)
S41–Ag1–Ag2	147.82(8)	N33–Ag3–Ag1	77.9(2)
N13–Ag1–Ag4	77.1(2)	S21–Ag3–Ag1	99.67(7)
Ag2–Ag1–Ag4	70.86(3)	N43–Ag4–S21	119.9(2)
S31–Ag1–Ag4	124.26(7)	N43–Ag4–S11	105.7(2)
S41–Ag1–Ag4	83.08(8)	P4–Ag4–S21	95.10(10)
Ag3–Ag1–Ag4	67.39(3)	P4–Ag4–S11	98.63(10)
N23–Ag2–S31	98.7(2)	N43–Ag4–P4	116.1(2)
P2–Ag2–S31	103.41(10)	S21–Ag4–S11	119.38(9)
S11–Ag2–S31	122.78(9)	N43–Ag4–Ag1	69.8(2)
S11–Ag2–Ag1	76.43(6)	P4–Ag4–Ag1	168.37(7)
N23–Ag2–P2	122.4(2)	S21–Ag4–Ag1	89.85(7)
N23–Ag2–S11	113.6(2)	S11–Ag4–Ag1	69.81(7)
P2–Ag2–S11	97.36(10)	N43–C42–S41	125.3(8)
N23–Ag2–Ag1	102.89(19)	N33–C32–S31	124.2(9)
P2–Ag2–Ag1	131.85(8)	N23–C22–S21	126.9(8)

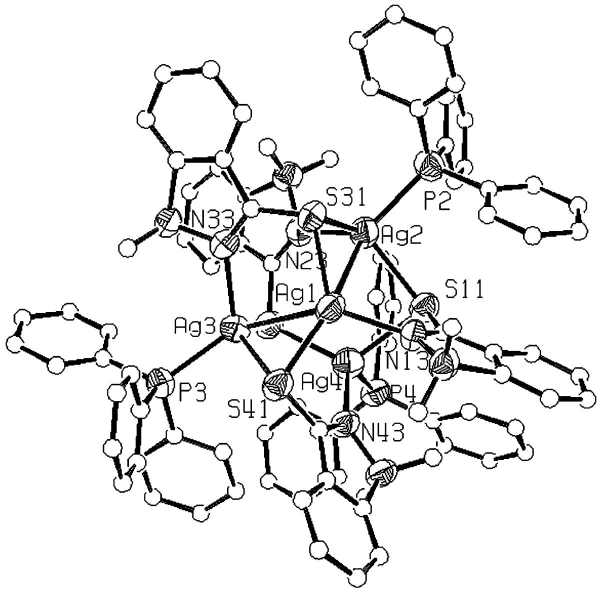


Fig. 3. ORTEP drawing of the molecular structure of [$Ag_4(tsac)_4(PPh_3)_3$] (**4**) showing 50% probability ellipsoids. Hydrogen atoms and some atom-labellings are omitted for clarity.

coordination of the anions, like in complex (**1**) with μ_3-*S*,*N* (η^2-*S*; η^1-*N*) type thiosaccharinates. The voids observed in the crystal structure are certainly large enough to house solvent molecules, however no solvent was found. It is assumed that the solvent was eliminated in transit and this also led to the larger *R*-value than the other two compounds.

4. Conclusion

Three new ternary silver(I) thiosaccharinate complexes were prepared and characterized showing three different coordination modes for the anion. When enough bulky P-donor ligands are involved a mononuclear Ag(I) centered complex results and monodentate S-donor thionate form is observed. When N,N-donor ligands are present, a dinuclear μ_2-S-thionate bridged complex can be produced. And when P-donor atoms are not enough to fill the coordination sphere of the metal atoms then a μ_3-N,S polynuclear complexes can be obtained.

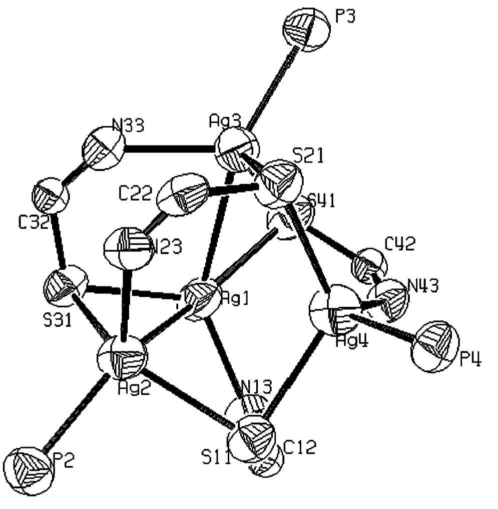


Fig. 4. ORTEP drawing of the metal centers and coordinated ligands inner atoms in complex [$Ag_4(tsac)_4(PPh_3)_3$] **(4)** showing 50% probability ellipsoids.

5. Supplementary material

Additional crystallographic data sets for the structures are available through the Cambridge Structural Data Base, as supplementary publication reference number CCDC-615246 for complex (2), CCDC-615245 for complex (3) and CCDC-615247 for complex (4). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: depositccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank SGCyT-UNS for financial support of Project M24/Q10. We express our gratitude to the generous assistance of Dr. Hugo de Lasa and his useful and stimulating discussions. We thank also Dra. Sandra Mandolesi for the register of NMR spectra and her helpful comments.

References

[1] (a) I.G. Dance, Polyhedron 5 (1986) 1037;
(b) B. Krebs, G. Henkel, Angew. Chem. Int. Ed. Engl. 30 (1991) 769;
(c) C. Housecroft, Coord. Chem. Rev. 115 (1992) 141;
(d) R.H. Holm, P. Kennepohl, E.I. Solomon, Chem. Rev. 96 (1996) 2239.

[2] (a) M. Hong, W. Su, R. Cao, W. Zhang, W.T. Wong, J. Lu, Inorg. Chem. 38 (1999) 600;

(b) M.C. Hong, Y.Z. Zhao, W.P. Su, R. Cao, M. Fujita, Z.Y. Zhou, A.C.S. Chan, Angew. Chem. Int. Ed. Engl. 39 (2000) 2468;
(c) W. Su, M. Hong, J. Weng, Y. Liang, Y. Zhai, R. Cao, Z. Zhou, A.S.C. Chan, Inorg. Chim. Acta 331 (2002) 8.

[3] (a) J.A. García-Vázquez, A. Souza-Pedrares, M. Carobel, J. Romero, A. Souza, Polyhedron 24 (2005) 2043, and refs. therein;
(b) J.A. García-Vázquez, J. Romero, A. Souza-Pedrares, M. Louro, A. Souza, J. Zubieta, J. Chem. Soc. Dalton Trans. (2000) 559.

[4] (a) E.S. Rapper, Coord. Chem. Rev. 153 (1996) 199;
(b) E.S. Rapper, Coord. Chem. Rev. 165 (1997) 475;
(c) J.A. García-Vázquez, J. Romero, A. Sousa, Coord. Chem. Rev. 193–195 (1999) 691;
(d) P.D. Akrivos, Coord. Chem. Rev. 181–210 (2001) 213.

[5] (a) S.H. Tarulli, O.V. Quinzani, O.E. Piro, E.J. Baran, E.E. Castellano, Monats. Chem. 132 (2001) 779;
(b) S.H. Tarulli, O.V. Quinzani, O.E. Piro, E.J. Baran, Z. Anorg. Allg. Chem. 628 (2002) 751;
(c) S.H. Tarulli, O.V. Quinzani, O.E. Piro, E.J. Baran, J. Mol. Struct. 656 (2003) 161;
(d) S.H. Tarulli, O.V. Quinzani, O.E. Piro, E.E. Castellano, E.J. Baran. J. Mol. Struct. 797 (2006) 56 (accesible on-line).;
(e) S.H. Tarulli, O.V. Quinzani, O.E. Piro, E.E. Castellano, E.J. Baran, Z. Anorg Allg. Chem. 629 (2003) 1975;
(f) M. Vieytes, D. Gambino, M. González, H. Cerecetto, S.H. Tarulli, O.V. Quinzani, E.J. Baran, J. Coord. Chem. 59 (2006) 102.

[6] E.J. Baran, V.T. Yilmaz, Coord. Chem. Rev. 250 (2006) 1980.

[7] G.P. Tellería, M. Dennehy, S.H. Tarulli, O.V. Quinzani, G. Echeverría, O.E. Piro, E.E. Castellano, in preparation.

[8] (a) A. Cassel, Acta Cryst. B 37 (1981) 229;
(b) D.E. Hibbs, M.B. Hursthouse, K.M.A. Malik, M.A. Beckett, P.W. Jones, Acta Cryst. C 52 (1996) 884.

[9] M.I. Bruce, D.N. Duffy, Aust. J. Chem. 39 (10) 1691.

[10] L.S. Ahmed, J.R. Dilworth, J.R. Miller, N. Wheatley, Inorg. Chim. Acta 278 (1998) 229.

[11] C. López, J.P. Fackler, R. Staples, S. Wang, R. Winpenny, Croat. Chem. Acta 68 (1995) 793.

[12] P.J. Cox, P. Aslanidis, P. Karagiannidis, S. Hadjikakou, Inorg. Chim. Acta 310 (2000) 268.

[13] P. Karagiannidis, P. Aslanidis, S. Kokkou, C.J. Cheer, Inorg. Chim. Acta 172 (1990) 247.

[14] G.A. Bowmaker, A. Effendy, S. Marfuah, B.W. Skeleton, A.H. White, Inorg. Chim. Acta 358 (2005) 4371.

[15] S. Schibye, R.S. Pedersen, S.O. Lawesson, Bull. Soc. Chim. Belges 87 (1978) 229.

[16] A. Vogel, Textbook of Practical Organic Chemistry, Longman Group Limited, London, 1978.

[17] G.M. Sheldrick, SHELXTL-01, Programs for Crystal Structural Analysis, University of Göttingen, Germany, 2001.

[18] O. Grupče, M. Penavić, G. Jovanovski, J. Chem. Crystallog. 24 (1994) 581.

[19] M.M. Branda, N.J. Castellani, S.H. Tarulli, O.V. Quinzani, E.J. Baran, R.H. Contreras, Int. J. Quant. Chem. 89 (2002) 525.

[20] (a) Y.I. Binev, C. Petkov, L. Pejov, Spectrochim. Acta Part A 56 (2000) 1949;
(b) G. Jovanovski, A. Cahil, O. Grupče, L. Pejov, J. Mol. Struct. 784 (2006) 7.

[21] E.J. Baran, O.E. Piro, J. Zinczuk, Z. Anorg. Allg. Chem. 632 (2006) 437.

[22] (a) R.J.H. Clark, C.D. Flint, A.J. Hempleman, Spectrochim. Acta Part A 43 (1987) 805;
(b) R. Pilk, F. Duschek, C. Fickert, R. Finsterer, W. Kiefer, Vibrat. Spectrosc. 14 (1997) 189.

[23] R.G. Inskeep, J. Inorg. Nucl. Chem. 24 (1962) 763.

[24] C. Kutal, Coord. Chem. Rev. 99 (1990) 213.

[25] E.L. Muetterties, C.W. Alegranti, J. Amer. Chem. Soc. 94 (1972) 6386.

[26] I. Beloso, J. Castro, J.A. García-Vázquez, P. Pérez-Lourido, J. Romero, A. Souza, Inorg. Chem. 44 (2005) 336.

[27] A. Vertova, I. Cucchi, P. Fermo, F. Porta, D.M. Proserpio, S. Rondinini, Electrochim. Acta (2006), doi:10.1016/j.electacta.2006.09.035.

[28] (a) C. Pettinari, Polyhedron 20 (2001) 2755;
(b) Z. Yuan, N.H. Dryden, J.J. Vittal, R.J. Puddephatt, Chem. Mater. 7 (1995) 1696.

[29] P. Aslanidis, S. Divanidis, P.J. Cox, P. Karagiannidis, Polyhedron 24 (2005) 853.

[30] D. Coucouvanis, N.C. Benzinger, S.M. Johnson, Inorg. Chem. 13 (1974) 1191.

[31] D.D. Heindrich, J.P. Fackler Jr., P. Lahuerta, Inorg. Chim. Acta 116 (1986) 15.

[32] N.B.N. Greewood, A. Earnshaw, Chemistry of the Elements, Pergamon, Oxford, UK, 1989, p. 1368.

[33] P. Pyykkö, Chem. Rev. 97 (1997) 597.

[34] M. Jansen, Angew. Chem. Int. Ed. 26 (1987) 1098.

[35] (a) I.G. Dance, L.J. Fitzpatrick, A.D. Rae, M.L. Scudder, Inorg. Chem. 22 (1983) 3785;
(b) I.G. Dance, L.J. Fitzpatrick, D.C. Craig, M.L. Scudder, Inorg. Chem. 28 (1989) 1853.

[36] M. Shi, J.K. Jiang, Chirality 15 (2003) 605.

[37] R. Noguchi, A. Mara, A. Sugie, K. Nomiya, Inorg. Chim. Acta 278 (1998) 229.

[38] P.C. Zachariadis, S.K. Hadjikakou, N. Hadjiliadis, A. Michaelides, S. Skoulika, Y. Ming, Y. Xiaolin, Inorg. Chim. Acta 343 (2003) 361.